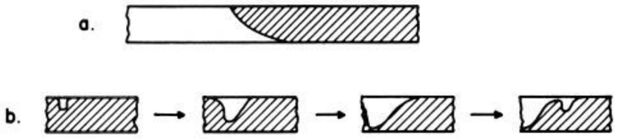

Figure 8. Schematic illustration of (a) the stable smooth and (b) the unstable "rolling" wave in a horizontal thick (i.d., = 4.76 mm) tube. ($[ClO_2^-]$ = 0.009 M, $[S_2O_3^{2-}]$ = 0.0045 M, $[OH^-]$ = 0.002 M.)

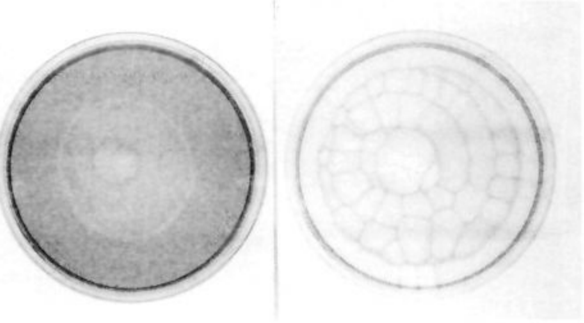

Figure 9. Concentric rings and mosaic patterns in a horizontal Petri dish (see text).

shape of the resulting front is the mirror image of the stable front. This front is unstable, and when the upper reacted portion cools, a new drop is formed, starting from the top of the tube again, as illustrated in Figure 8b. Thus one observes a "rolling" chemical wave, whose overall velocity is about 3–4 times higher than that of the stable front (Figure 8a). The "rolling" wave leaves behind unreacted zones, which slowly disappear. Exactly the same process takes place if the wave is initiated in the quasi-two-dimensional horizontal Petri dish, with the same thickness and reagent concentrations. In this case, however, concentric rings remain unreacted behind the front. The production of concentric rings in a reaction mixture which is neither oscillatory nor excitable is a striking demonstration of the importance of considering convective effects when investigating traveling waves. The slowly disappearing rings can also leave a mosaic pattern reminiscent of those reported by Avnir et al.[22] Both the concentric ring and mosaic patterns are illustrated in Figure 9.

Finally, temperature and density measurements in the arsenite–iodate system show that the reaction is exothermic and is accompanied by a *decrease* in the isothermal density. In this system, therefore, both effects act in the same direction. Thus the upward velocity should exceed the downward velocity for all concentrations.

Conclusion

The results presented in this paper argue strongly that previous chemical wave studies should be reanalyzed to assess the possible results of reaction exothermicity, convection, and heat conduction. This fact should be kept in mind by those studying chemical instabilities in unstirred spectrophotometer cells. As several groups[23–25] have shown in the case of photochemical oscillators, it is remarkably difficult to eliminate convection.

Perhaps the most surprising result in the present investigation is the magnitude of the isothermal density changes which takes place in the reactions studied. By taking account of this phenomenon we have been able to construct a model which reconciled the apparently contradictory results in the Fe^{2+}–HNO_3 and ClO_2^-–$S_2O_3^{2-}$ experiments and even allowed us to "invert the pumpkin" in the chlorite–thiosulfate velocity distributions. The "rolling waves" and concentric rings provide further support for the model.

More quantitative treatments of the phenomena discussed here are clearly called for, but they are likely to be extremely complex. Designing experiments to avoid or at least to minimize gravitational effects may be a more attractive option. While one might consider experiments in gravitation-free orbit, the use of sufficiently thin tubes would seem to provide a more accessible and less expensive solution to this problem.

Acknowledgment. This work was made possible by a U.S–Hungarian Cooperative Grant from the National Science Foundation (INT-8217658) and the Hungarian Academy of Sciences. It was also funded in part by Grant No. CHE-8419949 from the National Science Foundation to Brandeis University. We thank Kenneth Kustin for helpful discussions and William Shea for taking the photographs. We are especially indebted to Prof. Arne Pearlstein for enlightening conversations about hydrodynamics.

Registry No. Fe^{2+}, 15438-31-0; HNO_3, 7697-37-2; ClO_2^-, 14998-27-7; $S_2O_3^{2-}$, 14383-50-7.

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(21) Note that although the initial concentrations of ClO_2^- and $S_2O_3^{2-}$ do not appear explicitly in eq 3, they influence the wave velocity via their effect on $[H^+]_b$.

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Valence and Molecular Structure

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Abstract: The relation between bond valence and stability of molecules is further investigated. Different geometrical arrangements of molecules are compared with respect to valence, charge, occupation numbers, and total energy. It is demonstrated that the ionicity of molecules can be described by the bond number resulting from atomic valence numbers. It is also shown that ideas of bonding expressed in the recent molecular orbital valence bond (MOVB) theory can be quantified with valence.

1. Introduction

Many years ago, Pauling[1] advocated an explanation of the structure of molecules by valence bond theory. In this theory it is natural to attach special meaning to each of the bonds and consider the whole molecule in terms of its bond properties. One of the questions that arises is the problem of the partial ionic character of covalent bonds. The amount of ionic character is determined by the importance of the ionic structure in the total

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wave function. To assess the bond energy due to ionic character of a diatomic molecule AB, Pauling suggested to take the excess energy Δ over the average energy of the normal covalent bonds of the corresponding homomolecular diatomics AA and BB as a measure (eq 1.1). Taking the positive sign for E, it could be

$$\Delta = E_{AB} - \tfrac{1}{2}(E_{AA} + E_{BB}) \tag{1.1}$$

shown that Δ is positive in hydrogen halogenides and halogen halogenides. This means that reactions of the type in eq 2.2 are exothermic for the above compounds. For alkali hydrides,

$$A_2 + B_2 \rightarrow 2AB \tag{1.2}$$

however, Δ is found to be negative. We have previously introduced the valence number of an atom as a basis for an assessment of the amount of covalent bonding in a molecule on the self-consistent-field (SCF)[2] and configuration interaction (CI) levels.[3]

These ideas will now be used for a combination with molecular orbital valence bond (MOVB) theory[4,5] to describe the ionicity of molecules, i.e., partial ionic character of all bonds.

2. Atomic Valence Number V_A

To assess the amount of covalent bonding in a molecule, the following procedure will be used.[3] The density operator P is defined as a projection operator of a configuration interaction (CI) wave function Ψ consisting of configurations Ψ_I built from molecular orbitals (MOs) ψ_i

$$P = |\Psi\rangle\langle\Psi| \tag{2.1}$$

with

$$\Psi = \sum_I A_I \Psi_I$$

From the density operator P all diatomic portions of the following form are selected

$$P^{AB} = \tfrac{1}{2}\{|\Psi^A\rangle\langle\Psi^B| + |\Psi^B\rangle\langle\Psi^A|\} \tag{2.2}$$

The molecular orbitals ψ_i of the configurations Ψ_I are equally reduced to the diatomic form in eq 2.3.

$$\psi_i^{AB} = \psi_i^A + \psi_i^B \tag{2.3}$$

The covalent contributions to the bond AB between atoms A and B can now be defined as the expectation value of reduced density operator P^{AB} over all reduced MOs ψ_i^{AB} with occupation number n_i (eq 2.4). Direct evaluation of the bond valence V_{AB} leads to eq 2.5, derived in abbreviated form.

$$V_{AB} = \sum_i^{occ} n_i \langle\psi_i^{AB}|P^{AB}|\psi_i^{AB}\rangle \tag{2.4}$$

$$V_{AB} = \tfrac{1}{2}\sum_i^{occ} n_i[\langle\psi_i^A|\Psi^A\rangle\langle\Psi^B|\psi_i^B\rangle + \langle\psi_i^B|\Psi^B\rangle\langle\Psi^A|\psi_i^A\rangle] = \sum_i^{occ} n_i \sum_j^{occ} \langle\psi_i^A|\psi_j^A\rangle\langle\psi_j^B|\psi_i^B\rangle \tag{2.5}$$

Expansion of the MOs ψ_i in Schmidt and Löwdin[6] orthogonalized atomic orbitals (AOs) λ (eq 2.6) finally yields the form of eq 2.7. This latter form could be obtained in a heuristic fashion on the self-consistent-field (SCF) level.[2]

$$\psi_i = \sum_\rho c_{i\rho}\lambda_\rho \tag{2.6}$$

$$V_{AB} = \sum_{\mu,\nu} (P_{\mu\nu}^{AB})^2 \tag{2.7}$$

with

$$P_{\mu\nu}^{AB} = \sum_i^{occ} n_i c_{i\mu}^A c_{i\nu}^B$$

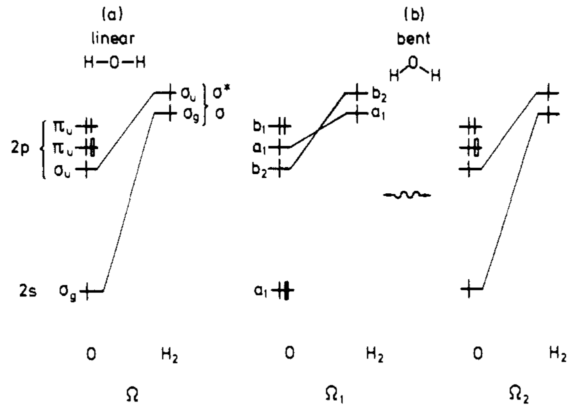

Figure 1. MOVB diagrams for the bonding in linear (Ω) and bent (Ω_1, Ω_2) water.

The atomic valence number V_A is given as the sum over all diatomic bond valences referring to atom A (eq 2.8). The total covalent bonding in a molecule can be characterized by the bond number M which is half the sum over all atomic valence numbers V_A (eq 2.9). From eq 2.7 it is apparent that bond valences are

$$V_A = \sum_{B \neq A} V_{AB} \tag{2.8}$$

$$M = \tfrac{1}{2}\sum_A V_A \tag{2.9}$$

quadratic in diatomic density matrix elements, whereas bond orders are linear. The advantage of bond valences over bond orders is that the former are additive, whereas the latter are not. The total covalent bonding can be represented as a sum of bond valences but not of bond orders. Bond valences are exclusive and refer to only one bond, whereas bond orders are in general inclusive and portions refer also to other bonds. Since we use orthogonalized orbitals, no immediate comparison with overlap populations is possible.

3. Relation to MOVB Theory

We wish to connect these ideas now with MOVB theory. There are several ways to reduce the atomic valence numbers V_A: (a) The "ionicity" of one or more interfragmental bonds, i.e., the bonds connecting two fragments, F_1 and F_2, is increased. We call this effect *interfragmental relaxation.* (b) One electron is demoted from a higher (u) to a lower (d) orbital *within* one fragment, e.g., F_1, so that interfragmental bonding (by means of electron pairing) must now be effected by u rather than by d. That is to say, there is a configurational change of the $u^2d^1 \rightarrow u^1d^2$ type in F_1, where the superscripts are the number of electrons. If F_1 is a first-row atom, u = 2p and d = 2s, the latter binds much more strongly than the former, and as a result, deexcitation is accompanied by loss of interfragmental bond strength. We call this deexcitation *intrafragmental relaxation* recognizing that, in molecules containing first-row atoms, *this may be an energy-lowering or energy-raising effect depending on which of the two factors (deexcitation or bond strength reduction) is more important.* As one of us has pointed out,[4] this is the basis of stereochemical diversity and the breakdown of the so-called "isoelectronic principle".[7] Furthermore, we recognize that intrafragmental relaxation will change the way in which atoms within a fragment, as well as atoms belonging to different fragments, are bound; i.e., it changes their "valence", as this term is understood in a classical sense.

In chemical transformations, both inter- and intrafragmental relaxation may occur simultaneously and, thus, they may act cooperatively or antagonistically. The case is illustrated by the prototypical $D_{\infty h} \rightarrow C_{2v}$ conversion of H_2O, viewed as "O plus H_2". According to MOVB theory, linear water ($D_{\infty h}$) can be adequately represented by a bond diagram in which the 2s and σ fragment

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Table I. Dependence of Atom and Bond Properties on Structural Changes in Compounds with Strong Overlap Binding

molecule	symmetry	atom A	valence V_A	net charge Q_A	bond AB	bond valence V_{AB}	bond length R_{AB}, Å	bond no. M	binding energy E, hartree[c]
H_2O	C_{2v}	O	1.96	−0.30	OH	0.98	0.978	1.95	−0.3515
		H	0.98	0.15					
	$D_{\infty h}$	O	1.62	−0.64	OH	0.81	0.955	1.71	−0.2359
		H	0.90	0.32					
NH_3	C_{3v}	N	2.97	−0.29	NH	0.99	1.017	2.97	−0.4564
		H	0.99	0.10					
	D_{3h}	N	2.88	−0.42	NH	0.96	0.990	2.91	−0.4349
		H	0.98	0.14					
CH_4	T_d	C	4.00	−0.00	CH	1.000	1.087	4.00	−0.6556
		H	1.00	0.00					
	D_{4h}	C	2.98	−0.79	CH	0.746	1.076	3.41	−0.4242
		H	0.96	0.20					
C_2H_2	$D_{\infty h}$	C	3.97	−0.11	CC	2.99	1.218	4.96	−0.6328
		H	0.99	0.11	CH	0.98	1.052		
	D_{2h}	C	2.88	−0.30	CC	2.05	1.242	3.79	−0.4861
		H	0.91	0.30	CH	0.41	1.288		
C_2H_4	D_{2h}	C	3.99	0.01	CC	2.04	1.323	5.99	−0.8951
		H	1.00	−0.00	CH	0.97	1.076		
	C_{2v}	C	2.78	−0.21	CC	0.91	1.442		
		H[a]	0.99	−0.03	CH[a]	0.97	1.091	4.73	−0.6451
		H[b]	0.95	0.23	CH[b]	0.44	1.286		

[a] Cis. [b] Bridged. [c] 1 hartree = 627.46 kcal/mol.

orbitals define a significantly "ionic" bond (Figure 1a). By contrast, bent water (C_{2v}) is a resonance hybrid of two bond diagrams (always to a first approximation); the principal one has a 2p–σ (Figure 1b, Ω_1) rather than a 2s–σ bond (Figure 1b, Ω_2), and the former is much more "covalent" than the latter, a consequence of the spacing of the 2s and 2p levels of O. All this has happened because there is a one-electron 2p → 2s electron demotion in going from $D_{\infty h}$ to C_{2v} as can be seen by comparing diagrams Ω_1 and Ω_2 of Figure 1b; i.e., inter- and intrafragmental relaxation are, by definition, interrelated. MOVB theory then predicts that bent H_2O will have *less* interfragmental and *more* intrafragmental relaxation; i.e., the $D_{\infty}h \rightarrow C_{2v}$ transformation will be accompanied by an *increased* oxygen valence number V_A. At the same time, the 2s orbital occupation should also *increase*.[8]

A second example is the linear ($D_{\infty h}$) vs. bridged (D_{2h}) acetylene comparison. If C_2H_2 is thought of as "C_2 plus H_2", MOVB theory predicts that the linear form involves tetravalent carbon, while in the bridged form carbon tends to be divalent (i.e., *less* excited) because the D_{2h} symmetry of the latter forces intrafragmental C_2 deexcitation (Figure 2). At the same time, the "ionicity" of the interfragmental bond is not expected to change very significantly because of the smaller energy separation of the $1\sigma_u$ and $1\pi_u$ levels of C_2. Hence, we expect that the $D_{\infty h} \rightarrow D_{2h}$ transformation will be accompanied by a decreased carbon value for V_A.

4. Ionicity in Compounds with Strong Overlap Binding

Pauling's empirical finding that (1.2) is exothermic for hydrogen fluoride would therefore mean that the increased bond ionicity is related to greater stability. This argument could be generalized to larger than diatomic systems as the exothermic reaction $2H_2 + O_2 \rightarrow 2H_2O$ reveals. However, we shall show more generally in this section that Pauling's argument is of limited validity.

We have studied some simple hydrides in alternative geometries with SINDO1[9,10] and have collected valence, charge, bond length, bond number, and binding energy in Table I. The net charges in the table reveal that for linear H_2O the situation is more polar but less stable than for bent H_2O. This is contrary to Pauling's expectation. The same holds for planar NH_3 vs. pyramidal NH_3. In these cases the increased polarity is reflected in a reduction of the bond number M for the less stable geometries. If the bonds were completely covalent, one would expect bond numbers 2 for H_2O and 3 for NH_3, and this is not the case. The important thing here is that the variation of M is an index of the electronic reorganization accompanying a geometrical change and fully consistent with the MOVB prediction that *intrafragmental* relaxation is responsible for the greater stability of bent H_2O and pyramidal NH_3. The same conclusion has been reached on the basis of a careful MO theoretical analysis of the problem.[11]

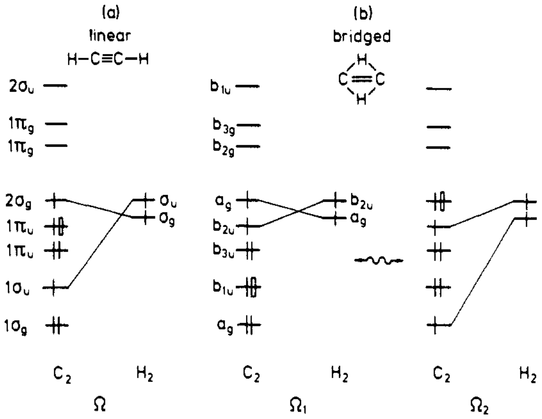

Figure 2. MOVB diagrams for the bonding of linear (Ω) and bridged (Ω_1, Ω_2) acetylene.

A much simpler case to understand is CH_4. Construction of the principal bond diagrams reveals that there is one less interfragmental bond in the planar form[4] consistent with a much reduced M value, if the system is viewed as C plus H_4. The change in bond ionicity is, of course, of secondary importance.

A word is in order about the argument that valence reduction in these molecules is simply a consequence of the fact that a bonding MO is converted into a nonbonding MO in the conversion of the more stable into the less stable geometry. In H_2O and NH_3 rehybridization could take place and still conserve the number of bonds and the bond valence if no increase in bond ionicity of the existing bonds would occur. In CH_4 this argument does not hold. Since indeed the total number of bonding electron pairs between C and the four H atoms is reduced to three in the planar form, bond polarity of the remaining three CH bonds cannot explain the valence number reduction. This simplest picture would result in a bond number $M = 3$. However, HH bonding among nearest neighbors and antibonding across the diagonal can and do increase the valence numbers of the H atoms in the planar form. This increases the bond number finally to 3.41.

Finally, an interesting case is the comparison of linear ($D_{\infty h}$) and bridged (D_{2h}) C_2H_2 (viewed as C_2 plus H_2) as well as that

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Table II. Dependence of Atom and Bond Properties on Structural Changes in Compounds with Weak Overlap Binding

molecule	symmetry	atom A	valence V_A	net charge Q_A	bond AB	bond valence V_{AB}	bond length R_{AB}, Å	bond no. M	binding energy E, hartree[c]
Li_2O	C_{2v}	O	2.25	-0.60	OLi	1.13	1.624	2.36	-0.2708
		Li	1.23	0.30					
	$D_{\infty h}$	O	2.26	-0.63	OLi	1.13	1.599	2.34	-0.2902
		Li	1.21	0.31					
Li_3N	C_{3v}	N	3.28	-0.58	NLi	1.09	1.732	3.70	-0.4023
		Li	1.37	0.19					
	D_{3h}	N	3.34	-0.62	NLi	1.11	1.711	3.70	-0.4193
		Li	1.35	0.21					
CLi_4	T_d	C	3.91	-0.57	CLi	0.98	1.944	4.75	-0.5423
		Li	1.40	0.14					
	D_{4h}	C	3.91	-0.57	CLi	0.98	1.965	4.80	-0.4915
		Li	1.42	0.14					
C_2Li_2	$D_{\infty h}$	C	3.75	-0.34	CC	2.71	1.215	4.80	-0.6553
		Li	1.05	0.34	CLi	1.29	1.897		
	D_{2h}	C	3.46	-0.34	CC	2.38	1.236	4.55	-0.7279
		Li	1.09	0.34	CLi	0.54	2.037		
C_2Li_4	D_{2h}	C	3.62	-0.20	CC	2.38	1.235	6.44	-0.8698
		Li	1.41	0.10	CLi	0.46	2.032		
	C_{2v}	C	3.54	-0.24	CC	2.34	1.243		
		Li[a]	1.52	-0.10	CLi[a]	0.38	2.158	6.19	-0.9126
		Li[b]	1.13	0.34	CLi[b]	0.35	2.164		

[a] Cis. [b] Bridged. [c] 1 hartree = 627.46 kcal/mol.

Table III. Changes of Occupation Numbers n, Total Bond Number M, and Binding Energy E (hartree[a])

no.	reactant	product	Δn_{1s} H	Δn_{2s} Li	Δn_{2p} Li	Δn_{2s} X	Δn_{2p} X	ΔM	ΔE
1	H_2O linear	H_2O bent	0.346			0.239	-0.585	0.25	-0.1156
2	NH_3 planar	NH_3 pyramidal	0.136			0.277	-0.413	0.06	-0.0215
3	CH_4 planar	CH_4 tetrahedral	0.802			0.065	-0.867	0.59	-0.2314
4	C_2H_2 bridged	C_2H_2 linear	0.390			-0.756	0.359	1.17	-0.1467
5	C_2H_4 bridged cis	C_2H_4 planar	0.426			-0.596	0.169	1.04	-0.2432
6	Li_2O linear	Li_2O bent		0.077	-0.048	0.032	-0.061	0.02	0.0193
7	Li_3N planar	Li_3N pyramidal		0.091	-0.052	0.046	-0.085	0.00	0.0169
8	CLi_4 planar	CLi_4 tetrahedral		0.070	-0.076	-0.006	0.013	-0.04	-0.0508
9	C_2Li_2 bridged	C_2Li_2 linear		0.047	-0.048	-0.208	0.209	0.25	0.0726
10	C_2Li_4 bridged cis	C_2Li_4 planar		0.112	-0.038	-0.070	-0.004	0.25	0.0427

[a] 1 hartree = 627.46 kcal/mol.

of planar (D_{2h}) and doubly bridged (C_{2v}) C_2H_4 (viewed as C_2 plus H_4). In both cases, M is reduced upon bridging because carbon is transformed from tetravalent toward the limit of divalent. The key role of intrafragmental deexcitation of C_2 becomes apparent by noting that while bond polarity may change (C_2H_2) or remain constant (C_2Li_2), M is significantly reduced in both cases (see Table III). More specifically, C_2H_2 and C_2H_4 reduce bond valence and bond number by breaking of one CC π bond due to hydrogen bridging. These situations may be called diradicals in the generalized sense.[12] It is in line with this definition that carbon appears in the calculation as trivalent, so the MOVB limit of divalent carbon is not reached. The reason why intrafragmental relaxation accompanying $D_{\infty h} \rightarrow C_{2v}$ transformation in H_2O is favorable while that accompanying the $D_{\infty h} \rightarrow D_{2h}$ change in C_2H_2 is unfavorable has been explained in the original monograph.[4]

5. Ionicity in Compounds with Weak Overlap Binding

It is now interesting to see how the situation changes when the hydrogen atoms are replaced by lithium. The diffuse orbitals and low electronegativity of lithium give rise to weak overlap binding. Pauling already recognized the difference in reaction 1.2 for alkali hydrides which is endothermic for these compounds. Table II contains valence, net charge, bond length, bond number, and binding energy for alternative geometries of lithium compounds based on SINDO1 calculations. The bond angle for symmetry C_{2v} of Li_2O was chosen as 105.2°, the same as in bent water, and 106.7° for pyramidal Li_3N, the same as in ammonia. The effects of geometry changes are attenuated in the lithium compounds compared to the hydrogen compounds, because the situation is very ionic. Li_2O and Li_3N are more stable in the linear and planar forms.

Because of the large bond ionicity, bond valences and bond numbers show very little or no changes. For CLi_4 the tetrahedral form is still more stable, but neither charges nor valences reflect this. The HOMO of the planar form of CLi_4 is a π orbital which extends bonding from C to all Li atoms. In this case σ bonding of the tetrahedral form is partially converted into π bonding, which in practice leaves the total valence number of carbon unchanged. The only indication for the increased stability is the contraction of bond lengths in these forms. Finally, and most important, in C_2Li_2 and C_2Li_4 a decrease in covalent bonding, indicated by bond valence and bond number, is accompanied by *stabilization*, in contrast to the hydrogenic systems.

Here we would like to mention that extensive ab initio calculations exist by Schleyer and his group on Li_2O,[13] Li_3N,[14] CLi_4,[14,15] C_2Li_2,[16,17] and C_2Li_4[18] on various levels of sophistication. Our study has an emphasis on the qualitative comparison of strong and weak overlap binding and does not compete with the numerical accuracy of some of these calculations, but the trends are the same in our SINDO1 calculations. For C_2Li_4 we find as the global

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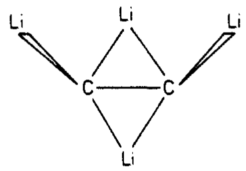

Figure 3. Global minimum structure of C_2Li_4 with bridging Li atoms in plane (MOVB), below plane (SINDO1), and above plane (4-31G).

minimum a doubly bridged structure with two Li in the cis position. Similar structures are predicted by MOVB theory[5] and 4-31G calculations by Jemmis, Kos, Pople, and Schleyer.[18] The difference is that MOVB suggests the bridged portion to be planar (Figure 3), whereas we find it slightly nonplanar with the two bridging Li folding down away from the two Li in the cis position, and Schleyer's calculations suggest a nonplanar bridged structure with the bridging Li folding up toward the cis Li atoms. Here MOVB theory interprets the bonding between the C_2 and Li_4 fragments by a dominant $(C_2)^-(Li_4)^+$ configuration with three bonds between the fragments which result from minimization of the excitation energy.

6. Occupation Numbers and Structure

In Table III we have collected the changes in occupation numbers *n* together with the changes of bond number and binding energy for the previous compounds. The energy differences can be compared with available ab initio calculations on the STO-3G, 3-21G, or 6-31G* level.[19] It is apparent from such a comparison that the relative stabilities are all qualitatively correct. Since it is not the purpose of this work to dwell on the numbers, but rather on the trends, we shall not give a more detailed comparison with ab initio calculations.

In the process of stabilization, the p orbitals are depopulated in H_2O, NH_3, and CH_4 in favor of 2s or $1s_H$. H_2O and NH_3 illustrate the importance of *intrafragmental relaxation* in determining stereoselection in one class of molecules. In planar CH_4 there is charge transfer from H_4 to C. This charge transfer is avoided in the tetrahedral form. In C_2H_2 and C_2H_4 *intrafragmental excitation* leads to the global minimum. As a result 2s is depopulated and $1s_H$ or 2p is more populated. In all these hydrogenic species stability corresponds to a larger *M* value.

For the analogous lithium compounds these effects are much smaller. Stability is greater for the slightly more ionic compounds and corresponds to smaller *M* values. The key prediction of MOVB theory that replacement of a strong (e.g., H) by a weak (e.g., Li) overlap binder will reverse stereoselectivity by favoring core deexcitation (see Chapter 2 of ref 5) is nicely borne out by results shown in Table III. While the global minimum of C_2H_2 and C_2H_4 involves a highly excited C_2 core, C_2Li_2 and C_2Li_4 are more stable in the bridged form in which C_2 is deexcited. We note here that "classical" Coulomb effects can mask these overlap effects in Li_2O and Li_3N because their significance is enhanced (increased electronegativity difference between core and ligand) relative to carbon–lithium compounds. As an example, Li_2O would have a smaller angle than H_2O if "classical" Coulomb effects (Li^+- - -Li^+ repulsion) were nonexistent! The near-zero changes of *M* as a function in geometry in Li_2O and Li_3N, in contrast to the case of C_2Li_2 and C_2Li_4, are supportive of this statement.

Table IV.

molecule	transformation	ΔE	ΔM	Δn_{2s}
A				
H_2O	$D_{\infty h} \rightarrow C_{2v}$	−	+	+
H_3N	$D_{3h} \rightarrow C_{3v}$	−	+	+
B				
Li_2O	$D_{\infty h} \rightarrow C_{2v}$	+	0	+
Li_3N	$D_{3h} \rightarrow C_{3v}$	+	0	+
C				
C_2H_2	$D_{2h} \rightarrow D_{\infty h}$	−	+	−
C_2H_4	$C_{2v} \rightarrow D_{2h}$	−	+	−
D				
C_2Li_2	$D_{2h} \rightarrow D_{\infty h}$	+	+	−
C_2Li_4	$C_{2v} \rightarrow D_{2h}$	+	+	−

7. Conclusion

An appropriately defined index which can be explicitly computed is a testing device for a general theory of chemical bonding. Such is the case with the atomic valence number V_A and the molecular bond number *M*. They have been used here to test some predictions of MOVB theory regarding molecular electronic structure and ground-state stereoselectivity. The qualitative trends revealed by the SINDO1 calculations are shown in Table IV and are all consistent with the predictions of MOVB theory. They demonstrate that *neither valence nor occupation numbers* have a simple universal relationship with energetics. Most important, they provide support for the "induced deexcitation model" which is the basis for understanding the stereochemical differences of organic and isoelectronic main group compounds (C vs. D in Table IV), e.g., why HCCH is linear but HSiSiH is a C_{2v} "butterfly".[20]

In summary, the message of this paper is that valence and bond number can be used as an index of intrafragmental relaxation, *direct or indirect*. Thus, it is really because oxygen is partly deexcited in H_2O (C_{2v}) that the OH bonds are more "covalent" and *M* is larger, with an analogous situation existing in NH_3. In C_2H_2 and C_2H_4, carbon can be tetra- or divalent, or in-between, and this is what *M* measures. Note that oxygen remains always divalent, while carbon changes from tetravalent toward divalent in our comparisons.

Acknowledgment. The calculations were performed on the CYBER 76 at Universität Hannover.

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